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Reaction of Nitric Oxide and Silica-Attached Rhodium Carbonyl Complexes

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Abstract: Reaction of the silica-bound rhodium μ-oxo carbonyl complex **1** with NO at 100 °C resulted in the formation of the rhodium oxygen adduct **2** (80%) and rhodium nitrate/nitrite complex (20%). CO_2 formation was observed by IR analysis. Since no other nitrogen-containing products, particularly N_2O, either on the surface or in the gas phase, were observed, we propose that N_2 formation accounts for the remaining nitrogen. Increasing the reaction temperature to 400 °C resulted in the decomposition of the rhodium nitrate/nitrite complex and the appearance of a nitrosyl species which was characterized by an NO stretching frequency at 1890 cm^{-1}. Trace amounts of rhodium isocyanate, accounting for less than 2% of the total rhodium in the sample, were also produced. The carbonyl complex **1** was regenerated in both cases by reaction with CO at 100 °C; the rhodium nitrate/nitrite complex was unreactive toward CO.

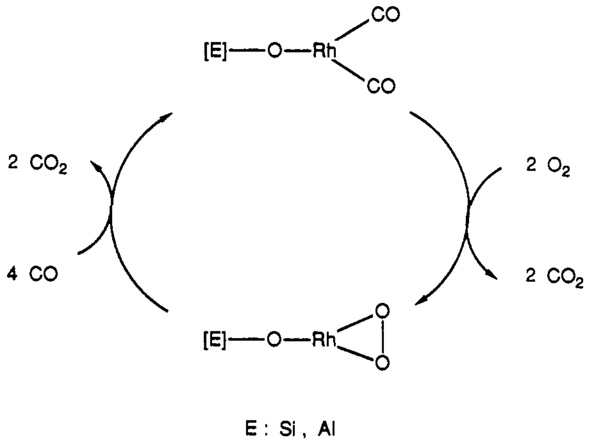
1. Introduction

Nitric oxide reduction and decomposition over rhodium have been extensively studied and reviewed.[1,2] In particular, there have been several investigations involving the reduction of nitric oxide by carbon monoxide over rhodium dispersed on metal oxide supports.[3-9] These investigations relied primarily upon infrared spectroscopy to characterize reaction products. While consistent results are reported from a given laboratory, there are variations concerning rhodium nitrosyl complex formation and reactivity in the results from different laboratories. Rhodium carbonate, nitrate, and isocyanate complex formation also varies widely from study to study.

We believe the variations are the result of differences in the method of preparation of the dispersed rhodium, differences that cannot be controlled and characterized at the molecular level. Generally, supported rhodium samples are prepared by wet impregnation of a complex (typically $RhCl_{3n}\cdot H_2O$) onto a metal oxide, followed by reduction at high temperature with dihydrogen. This is a complex process and differences in oxide pretreatment or reduction conditions may lead to samples of somewhat different dispersion and ligation. Unfortunately, the resulting rhodium samples cannot be characterized at a molecular level, so meaningful comparisons, which could account for the differences in reactivity, are precluded.

The use of organometallic complexes, in a controlled and characterizable fashion, is helpful in circumventing these difficulties. To this end and to establish the chemical transformations taking place on rhodium during the reduction of nitric oxide by carbon monoxide, we used the silica-attached rhodium μ-oxo carbonyl dimer ($([SiO]Rh(CO)_2)_2$ (**1**), a surface complex recently characterized at the molecular level by IR analysis of the ^{13}CO-enriched complex.[10] The surface carbonyl complex is a close structural analogue of $[Rh(CO)_2Cl]_2$;[11] both rhodium metal centers are attached to silica by covalent Rh–O bonds. It has been proposed that the oxygens that are covalently bonded to rhodium also bridge the two metal centers (Figure 1).[12] Reaction of the dimeric complex **1** with oxygen has been investigated by Schwartz and Fischer,[13] who chemically characterized the rhodium oxygen adduct ($([SiO]Rh(O_2))_2$ (**2**) by the stoichiometry shown in Scheme I. By utilizing complexes **1** and **2**, we can investigate the reactivity of rhodium for the reduction of nitric oxide at the molecular level, assuming the integrity of these complexes is maintained under the reaction conditions employed. Although we do not expect reactivity at the molecular level to be necessarily identical with that observed in previous studies of small particles, determination of this reactivity establishes a reference point from which comparisons between these highly dispersed molecular complexes and larger rhodium aggregates may provide insight about reaction pathways. We have demonstrated by IR and X-ray photoelectron spectroscopy (XPS) that the rhodium oxygen adduct **2** is the primary product resulting from the reaction between the μ-oxo carbonyl complex **1** and nitric oxide; rhodium nitrate/nitrite is formed as a side product, and at high temperatures detectable amounts of isocyanate are formed.

Scheme I



2. Experimental Section

1. X-ray Photoelectron Spectroscopy (XPS). Photoemission experiments were performed with a VG ESCALAB Mark I spectrometer system with a hemispherical analyzer and diffusion and titanium sublimation pumps. Pressures were typically in the low- to mid-10^{-10}-Torr range. The measurements were made with an unmonochromatized Mg Kα X-ray source. Binding energies were determined within an uncertainty of ±0.1 eV. The system also included an attached preparation chamber equipped with sample heating as well as CO, O_2, and NO gas handling lines. Reactions were performed in the preparation chamber.

2. Fourier Transform Infrared Spectroscopy (FTIR). Infrared spectra were recorded with a resolution of 4 cm^{-1} on a Mattson Cygnus 100 FTIR system. Unless otherwise stated, IR spectra were recorded at

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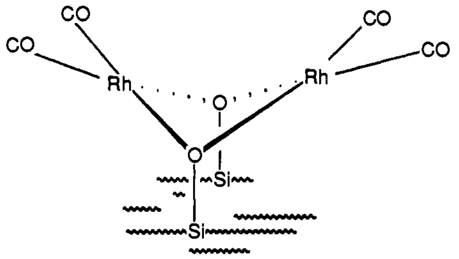

Figure 1. Proposed structure of the rhodium μ-oxo carbonyl complex **1**. The rhodium metal centers are bridged via two oxygen atoms attached to the silica surface; the carbonyl ligands are terminal [MCS].

ambient temperature. The infrared experiments were performed in a stainless steel ultrahigh vacuum (UHV) system partitioned by a gate valve into two chambers. One chamber is equipped with a double-pass cylindrical mirror analyzer (CMA) and a UTI 100C quadrupole mass spectrometer. The other, a preparation chamber, has two CaF windows (Harshaw) concentric with the infrared beam path which passes through the chamber to a mercury cadmium telluride (MCT) detector, enabling us to collect transmission spectra of the silica-supported complexes. External optics were continuously purged with dry nitrogen. The base pressure of the entire UHV system was 1×10^{-9} Torr; higher pressures in the preparation chamber were monitored by two MKS baratron capacitance manometers. Varian variable leak valves to each chamber from a common manifold enabled the dosing of volatiles to either chamber and the analysis of volatile mixtures in the preparation chamber by mass spectrometry. The manifold was independently evacuated from the UHV system.

3. Sample Preparation. The synthesis of the silica-attached rhodium bis(allyl) complex, ([SiO]Rh(allyl)$_2$)$_2$, from (RhC_3H_5)$_3$ and Aerosil 300 silica (Degussa) has been described previously;[10] 1.97 wt % rhodium was deposited. This material was stored in evacuated ampules until preparation for UHV XPS or FTIR experiments, at which point 25 mg was pressed into a highly transparent tantalum mesh (50 mesh, CPI Inc.) spot welded to two tantalum wires that led to a pair of insulated copper heating leads. The sample was resistively heated through the tantalum by an external power supply and conductively cooled by a liquid nitrogen reservoir above the sample. A chromel–alumel thermocouple spot welded to the tantalum mesh monitored the sample temperature. Sample manipulation in the UHV system has been previously described.[14]

Preparation of ([SiO]Rh(CO)$_2$)$_2$ (1). The silica-attached rhodium bis(allyl) complex in vacuo was exposed to 30 Torr of CO at ambient temperature for 2 h and then evacuated, yielding the rhodium μ-oxo carbonyl complex **1**. Water, adsorbed while handling the sample in air, was removed by gradually heating the initially formed **1** to 200 °C under 1×10^{-6} Torr of O_2. Retreatment of the sample with CO (30 Torr, 100 °C) resulted in **1** (Figure 3a). From FTIR, ν_{CO} = 2106 (sh), 2090 (s), and 2030 (s) cm^{-1}. From XPS, the binding energy of Rh 3d$_{5/2}$ = 309.5 eV.

Preparation of ^{13}CO-Enriched Samples. A mixture of $^{13}CO/^{12}CO$ was prepared, and an isotopic enrichment level of 33% (±2%) was determined by mass spectrometry. The sample was exposed to approximately 50 Torr of the mixture at 100 °C until no change was noted by IR in the course of 1 h. The sample was then evacuated and analyzed by IR.

Preparation of ([SiO]Rh(O$_2$))$_2$ (2). Species **1** was exposed to 30 Torr of O_2 at 100 °C for 2 h. Loss of carbonyl ligation to the rhodium metal center and the appearance of CO_2 was followed by IR. Evacuation resulted in the formation of **2** (Figure 3b). The binding energy of Rh 3d$_{5/2}$ = 310.0.

Reaction of 2 with CO. The rhodium oxygen adduct **2** was exposed to 30 Torr of CO at 100 °C for 1.5 h. Evacuation of the CO yielded **1** (Figure 3c).

Reaction of 1 with NO. The rhodium μ-oxo carbonyl complex **1** was exposed to 30 Torr of NO at 100 °C for 1 h. IR detected the rapid loss of carbonyl ligation to the rhodium metal center. Evacuation yielded **2** (the binding energy of Rh 3d$_{5/2}$ = 310.1), which was contaminated with rhodium nitrate/nitrite complex (ν_{NO} = 1538 cm^{-1}; Figure 4b).

At higher temperature (400 °C), reaction of **1** with 70 Torr of NO (2.5 h) resulted in the formation of a rhodium nitrosyl species (ν_{NO} = 1897 cm^{-1}; Figure 7c). Upon cooling to ambient temperature and evacuation, the intensity of the nitrosyl absorption decreased significantly (Figure 7d).

Regeneration of 1 after Exposure to NO at 100 °C. Reaction of the NO-treated rhodium sample with 30 Torr of CO (100 °C, 1.5 h) resulted in the formation of **1** upon evacuation. The rhodium nitrate/nitrite complex was unaffected by treatment with CO (Figure 4).

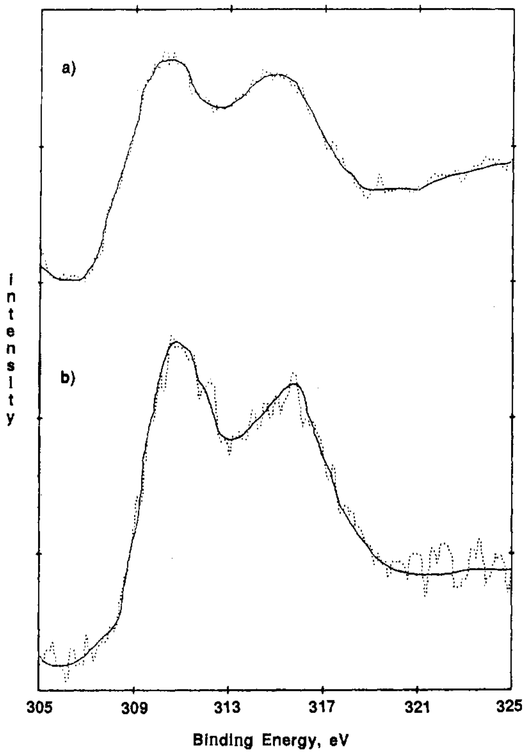

Figure 2. XPS spectra of Rh: (a) Sample of $Rh_2O_3{\cdot}nH_2O$ impregnated on Cabosil 200 M (3d$_{5/2}$ BE = 310.5 eV); (b) ([SiO]Rh(C_3H_5)$_2$)$_2$ that has been exposed to air at ambient conditions (3d$_{5/2}$ BE = 310.7 eV).

Table I. Rh 3d$_{5/2}$ Binding Energies

reaction	complex	BE, eV
([SiO]Rh(C_3H_5)$_2$)$_2$ + air	([SiO]Rh(O_2))$_2$/hydrated	310.7
	$Rh_2O_3{\cdot}nH_2O/SiO_2$	310.5
	([SiO]Rh(CO)$_2$)$_2$ (**1**)	309.5
([Si]–O–Rh(CO)$_2$)$_2$ + O_2	([SiO]Rh(O_2))$_2$ (**2**)	310.0
([Si]–O–Rh(CO)$_2$)$_2$ + NO	([SiO]Rh(O_2))$_2$ (**2**)	310.1
	Rh_2O_3[GMA]	310.2
	[Rh(CO)$_2$Cl$_2$][FAR]	309.7

3. Results and Discussion

1. Characterization of ([SiO]Rh(CO)$_2$)$_2$ (1) and ([SiO]Rh(O$_2$))$_2$ (2). A valid investigation of nitric oxide/carbon monoxide reactivity for the well-characterized silica-attached rhodium complexes required us to establish that the formation and reactivity of these complexes was unaffected by exposure to air. These complexes and their reactivity had previously been studied in moisture-free environments,[10] but in our system, transfer of ([SiO]Rh(allyl)$_2$)$_2$ to the UHV chamber involved exposure to air. In addition to adsorbing water, the silica-attached rhodium bis(allyl) complex reacted slowly with O_2, resulting in the loss of allyl ligand coordination to the rhodium metal center. Both effects were monitored by IR analysis. Extended exposure of the sample to air (1 week, ambient conditions) resulted in the loss of all allyl ligation to the metal center. The resulting rhodium complex was characterized by XPS (Figure 2) as the hydrated rhodium oxygen adduct **2**. The Rh 3d$_{5/2}$ binding energies of the air-exposed rhodium complex (310.7 eV) and a sample of $Rh_2O_{3n}{\cdot}H_2O$ (310.5 eV) dispersed onto silica by wet impregnation techniques are the same, within the range of uncertainty (Table I).

While either the silica-attached rhodium bis(allyl) complex or the hydrated rhodium oxygen adduct can serve as the precursor to the μ-oxo carbonyl complex **1**, it is important to dehydrate the silica sample before reaction with NO. If heated in the presence of water, complex **1** was transformed into an aggregated Rh species whose formation was signaled by the appearance of new terminal and bridging carbonyl absorptions in IR analysis.[15,16] Adsorbed

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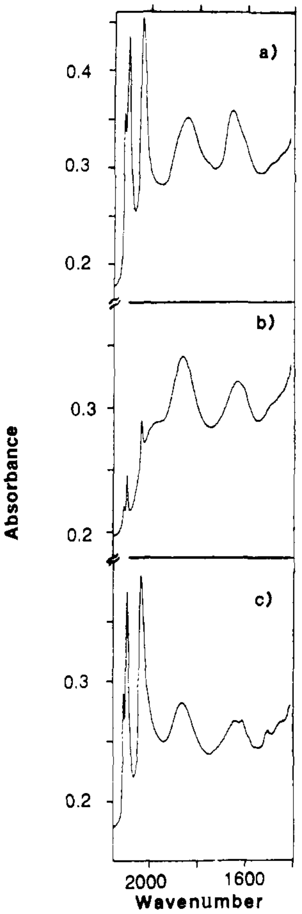

Figure 3. IR spectra of the reaction of rhodium μ-oxo carbonyl complex **1** with oxygen and subsequent regeneration by treatment with carbon monoxide: (a) rhodium μ-oxo carbonyl complex ($([SiO]Rh(CO)_2)_2$ (**1**); (b) rhodium oxygen adduct ($([SiO]Rh(O_2))_2$ (**2**) generated from the μ-oxo carbonyl complex (30 Torr of O_2, 100 °C, 2 h); (c) rhodium μ-oxo carbonyl complex regenerated from the oxygen add [illegible] (30 Torr of CO, 100 °C, 1.5 h).

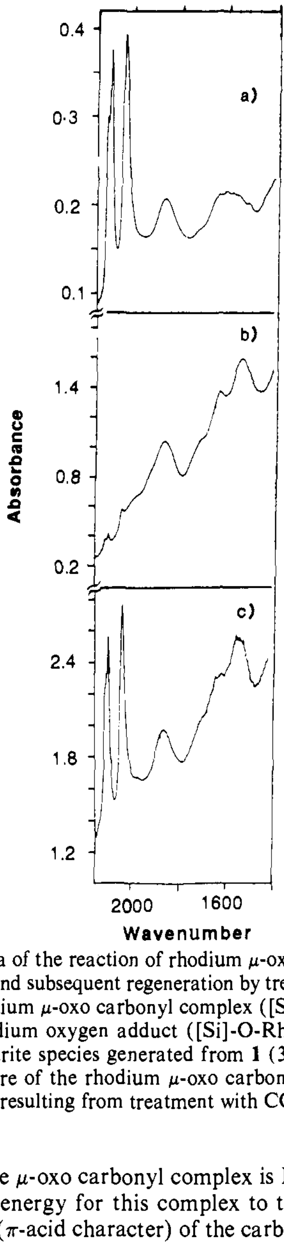

Figure 4. IR spectra of the reaction of rhodium μ-oxo carbonyl complex **1** with nitric oxide, and subsequent regeneration by treatment with carbon monoxide: (a) rhodium μ-oxo carbonyl complex ($([SiO]Rh(CO)_2)_2$; (b) mixture of the rhodium oxygen adduct ($[Si]\text{-}O\text{-}Rh(O_2))_2$ (**2**) and the rhodium nitrate/nitrite species generated from **1** (30 Torr of NO, 100 °C, 1 h); (c) mixture of the rhodium μ-oxo carbonyl complex and nitrate/nitrite species resulting from treatment with CO (30 Torr, 100 °C, 1.5 h).

water was removed from these silica-supported samples by heating the initially formed **1** under a constant flush of O_2. Subsequent treatment with CO (30 Torr, 100 °C) resulted in the formation of **1**, as determined by IR (Figure 3a). Further characterization of the carbonyl complex by IR was achieved via ^{13}CO enrichment.[17] The rhodium carbonyl complex that had been treated with a $^{13}CO/^{12}CO$ mixture (Figure 8a) had an IR spectrum nearly identical with that reported previously[10] for **1**, indicating the carbonyl complexes were the same.

The reactivity of the oxide-attached rhodium carbonyl complexes toward oxygen has been investigated.[13] The rhodium μ-oxo carbonyl complex reacts with O_2 to form an oxygen adduct (Scheme I) and can be regenerated by exposure to CO. IR analysis (Figure 3) demonstrated that the surface-attached rhodium complexes that we used also exhibited this behavior. There was no chemical or spectroscopic evidence suggesting that complexes **1** and **2** were different from those studied previously.[10,13]

Complexes **1** and **2** were further characterized by XPS (Figure 6a,b). The Rh $3d_{5/2}$ binding energies for the two complexes were 309.5 and 310.0 eV, respectively (Table I). The Rh $3d_{5/2}$ binding energy for **1** is similar to the binding energies reported for $[Rh(CO)_2Cl]_2$ (309.7 eV) and rhodium carbonyl species on alumina (309.45–310.2 eV).[18] The formal oxidation state of the rhodium metal center in the μ-oxo carbonyl complex is Rh^+; we attribute the high binding energy for this complex to the electron withdrawing capacity (π-acid character) of the carbonyl ligands. The rhodium oxygen adduct **2** has a Rh $3d_{5/2}$ binding energy similar to the value reported for anhydrous Rh_2O_3 (310.2 eV).[19] The binding energy for hydrated **2** (Figure 2b) is 0.7 eV higher than for dehydrated **2**. The same trend has been previously reported for Rh_2O_3, where the hydrated complex has a binding energy 1.0 eV higher than the anhydrous complex.[20] The formal oxidation state of the rhodium metal center of the oxygen adduct is Rh^{3+}.

2. Reaction of ($[SiO]Rh(CO)_2)_2$ (1) with NO. The addition of NO to the μ-oxo carbonyl complex **1** at 100 °C, which was continuously monitored by FTIR, resulted in a rapid decrease in carbonyl ligation and concomitant CO_2 formation (qualitatively the same results are obtained at 250 and 400 °C). No N_2O formation was observed by IR, suggesting that N_2 is the coproduct of this reaction, but mass spectrometry measurements were inconclusive because the maximum amount of product was only a few micromoles and not distinguishable above background. In contrast to previous investigators,[3-9] we observed no significant nitrosyl coordination to the rhodium metal center. After the reaction and evacuation of the chamber, IR analysis (Figure 4b) revealed a new absorption at 1538 cm^{-1} and residual **1**. The slight

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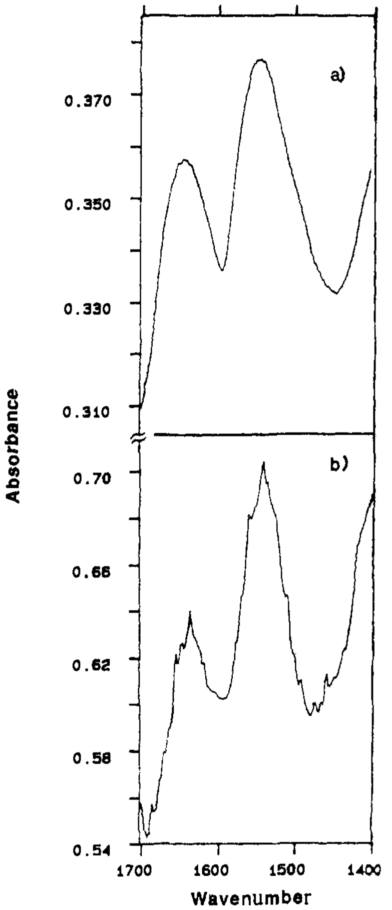

Figure 5. IR spectra of the nitrate/nitrite absorption resulting from the reaction of nitric oxide and rhodium μ-oxo carbonyl complex **1** (30 Torr of NO, 100 °C, 1 h): (a) nitrate/nitrite absorption from isotopically unenriched **1** (ν_{NO} = 1540.7 cm^{-1}); (b) nitrate/nitrite absorption from a 33% ^{13}CO-enriched (±2%) rhodium carbonyl complex (ν_{NO} = 1540.2 cm^{-1}).

broadening of the silica combination band at 1870 cm^{-1} may have been due to a nitrosyl species. Reaction of the sample with CO at 100 °C resulted in the re-formation of **1**; the absorption at 1538 cm^{-1} was not affected by CO (Figure 4c). The integrated area of the carbonyl absorptions of **1** decreased 20% in passing from Figure 4a to Figure 4c, suggesting that the new complex accounted for approximately 20% of the total rhodium deposited on the silica. Treatment of the sample with NO and CO sequentially six additional times did not alter significantly the ratio of the carbonyl complex **1** to the nitrate/nitrite species.

Arai and Tominaga observed an IR band at 1550 cm^{-1} which they assigned to rhodium nitrate/nitrite;[4] rhodium carbonates have also been assigned in this region.[3-5] To determine the identity of the 1538-cm^{-1} band in our experiments, we reacted ^{13}CO-enriched **1** with NO (Figure 5). Identical reaction conditions yielded neither additional absorptions nor broadening of the 1538-cm^{-1} absorption. We conclude from this observation that formation of the new complex via reaction with NO does not involve incorporation of the carbonyl ligands initially coordinated to rhodium. Since such incorporation would be expected for a carbonate species, we concur with Arai and Tominaga in assigning the absorption at 1538 cm^{-1} to a rhodium nitrate/nitrite species.

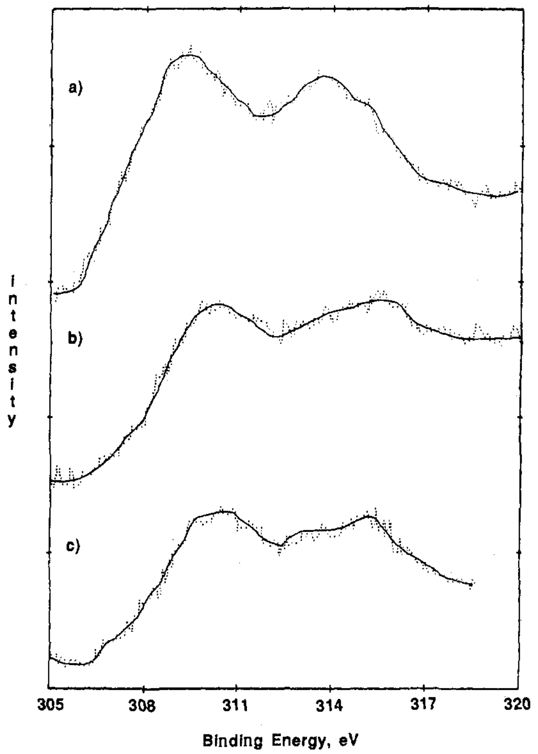

Figure 6. Rhodium 3d XPS spectra (3d$_{5/2}$ BE is given) of the μ-oxo carbonyl complex **1** and the oxygen adducts formed via reaction with oxygen and nitric oxide: (a) ([SiO]Rh(CO)$_2$)$_2$ (BE = 309.5); (b) rhodium oxygen adduct **2** resulting from reaction of the carbonyl complex with O$_2$ (BE = 310.0); (c) rhodium oxygen adduct **2** resulting from reaction of the carbonyl complex with NO (BE = 310.1).

The NO-treated sample was further characterized by XPS (Figure 6c). The binding energy for Rh 3d$_{5/2}$ was 310.1 eV (Table I). Only the dominant form of rhodium was detected. The rhodium nitrate/nitrite complex present in the NO-treated sample was not detected, due to its low concentration (20% of the total rhodium complexes, as discussed earlier). The combined XPS and IR data suggest that the rhodium oxygen adduct **2** was the primary product in the reaction of **1** and NO. Direct IR identification of **2** was impossible because the CaF_2 windows on the reaction chamber limited the IR transmission to 1100 cm^{-1}, and the silica support effectively increased the transmission limit to 1400 cm^{-1}. However, IR analysis demonstrated that rhodium nitrosyl complex formation was, at most, insignificant, and the reactivities of CO with the NO-treated sample and species **2** were nearly identical. The only difference was the presence of the rhodium nitrate/nitrite complex when NO was used. XPS data corroborated the assignment; the spectra of **2** (Figure 6b) and the NO-treated sample show similar peak shapes and identical binding energies, within experimental error.

3. Formation of a Nitrosyl Adduct. In several of the aforementioned investigations, the authors noted that heating the rhodium/metal oxide sample in the presence of NO induced the formation of a nitrosyl species.[3-5,8] This species, formed only at temperatures ≥200 °C, was characterized by IR analysis (ν_{NO} = 1890 cm^{-1}) only as Rh–NO$^+$.[21]

The reaction between ^{13}CO-enriched **1** (Figure 7a) and NO at 250 °C (Figure 7b) and at 400 °C (Figure 7c,d) was monitored continuously by IR. In the spectrum of the sample after treatment of **1** with 70 Torr of NO at 250 °C for 2 h and subsequent evacuation (Figure 7b), formation of the rhodium nitrate/nitrite complex (ν_{NO} = 1538 cm^{-1}) and unreacted ^{13}CO-enriched **1** were evident. Two new absorptions at 1835 and 1733 cm^{-1} corresponded to those previously identified as belonging to a rhodium bis(nitrosyl) species.[8] Subsequent treatment with CO (30 Torr, 100 °C) resulted in a spectrum identical with that in Figure 4c. Figure 7c shows the spectrum of the sample after 2.5 h under 70 Torr of NO at 400 °C. The absorptions due to the rhodium bis(nitrosyl) and nitrate/nitrite species have disappeared, and a new absorption at 1897 cm^{-1} (assigned to linearly coordinated NO) dominates the spectrum. Uncoordinated NO was responsible for the sharp absorption at 1876 cm^{-1}. Evacuation of the reaction chamber resulted in both a sharp decrease in intensity of the 1897-cm^{-1} absorption and the appearance of new absorptions at 2083 and 1503 cm^{-1} (Figure 7d), neither of which had been previously

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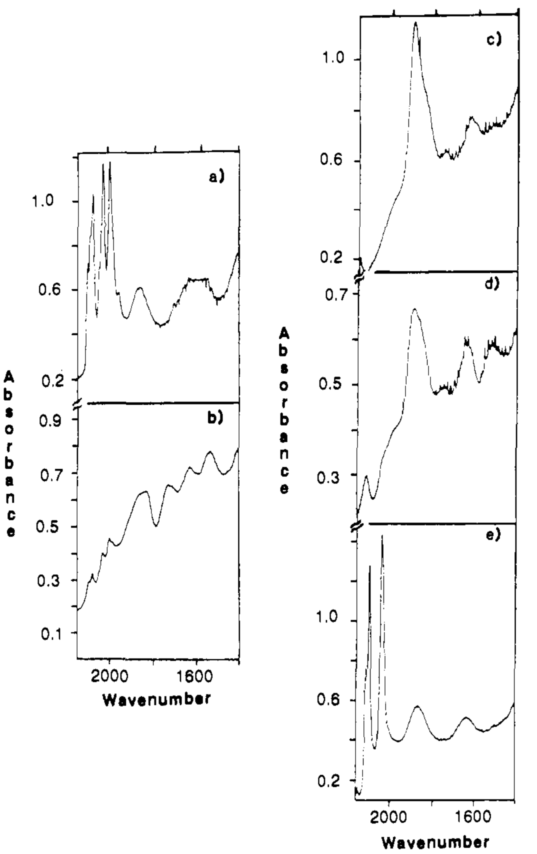
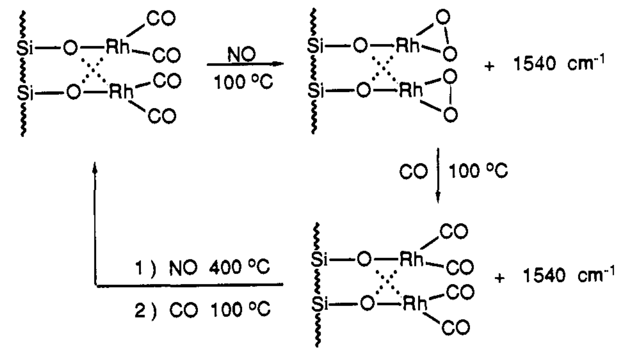


Figure 7. IR spectra of the reaction of ^{13}CO-enriched rhodium μ-oxo carbonyl complex **1** with nitric oxide at elevated temperatures: (a) ^{13}CO-enriched **1**; (b) sample after reaction of the carbonyl complex with NO at 250 °C (70 Torr, 2 h) resulting in nitrosyl complexation (ν_{NO} = 1835.3, 1733.4 cm^{-1}) and nitrate/nitrite formation (ν_{NO} = 1538.4 cm^{-1}); (c) sample under 70 Torr of NO at 400 °C (2.5 h) (ν_{NO} = 1897.1 cm^{-1}); (d) sample reacted with NO at 400 °C upon evacuation (ν_{NO} = 1896.3 cm^{-1}); (e) **1** regenerated upon treatment of (d) with CO (30 Torr, 100 °C, 1.5 h).

Scheme II



observed; neither was characterized. Treatment of the sample with CO (Figure 7e) resulted in the formation of the rhodium μ-oxo carbonyl complex **1**, contaminated by a trace amount (less than 2% based on loss of carbonyl) of isocyanate complex (ν_{NCO} = 2204 cm^{-1}). No absorption due to the rhodium nitrate/nitrite complex remained. Arai and Tominaga also observed the decomposition of this species at 400 °C.[4]

^{13}CO enrichment of the resulting carbonyl complex which had been exposed to NO at 400 °C yielded an IR spectrum identical with that of the ^{13}CO-enriched starting complex **1** (Figure 8). Thus, IR analysis demonstrated that no net change occurred in the coordination of the oxide surface to the rhodium metal center as a result of the sequence of reactions outlined in Scheme II.

4. Coordination of NO to Silica-Attached Rhodium Complexes. While earlier studies employed wet impregnation of rhodium complexes to deposit the rhodium onto the metal oxide surface, the rhodium complexes in this study are attached covalently via chemical reaction with surface hydroxyl groups.[10] This results in significantly different chemistry toward NO. At ambient temperatures, NO neither reacts with nor coordinates to the carbonyl complex **1**. When NO reacts with the rhodium μ-oxo carbonyl complex **1** at 100 °C, the reaction is immediate and the rhodium oxide adduct **2** and a rhodium nitrate/nitrite species form. No significant nitrosyl ligation to rhodium was observed by IR. Preliminary EXAFS analysis of **2** suggested the rhodium complex to be coordinatively unsaturated; five Rh–O bonds were characterized, with three of these originating from the metal oxide.[22] In light of the facile coordination of water to **2** and its reactivity toward CO (vide supra), it is unlikely that inaccessibility of NO to the rhodium metal center explains the lack of nitrosyl ligation, and we conclude, therefore, that **2** is unreactive toward NO at 100 °C.

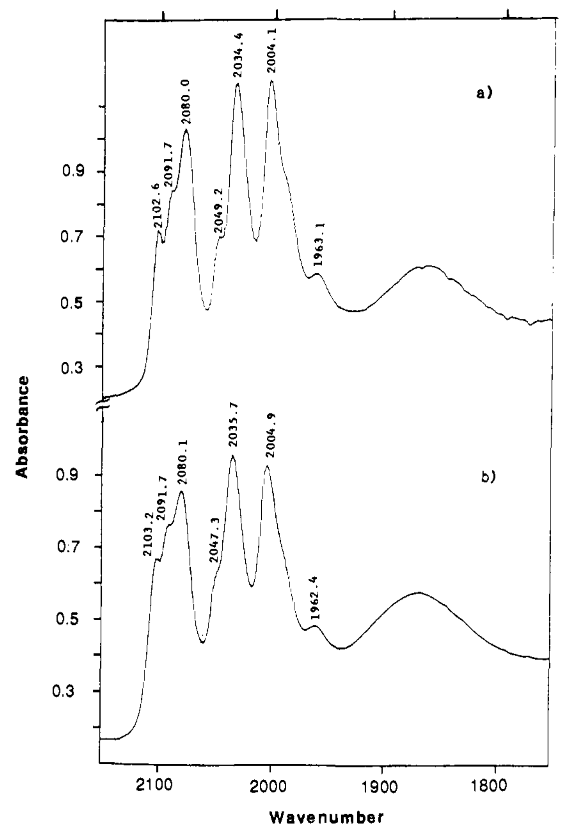


Figure 8. IR spectra of 33% ^{13}CO-enriched rhodium μ-oxo carbonyl complexes: (a) initial rhodium carbonyl complex **1**; (b) rhodium carbonyl complex **1** regenerated after reaction with nitric oxide at 400 °C.

The origin of the nitrosyl species formed at 400 °C under 70 Torr of NO is unclear. Since only IR characterization was done, we cannot estimate how much of the total rhodium in the sample is accounted for by this complex. Concomitant with the appearance of the nitrosyl species is the disappearance of the rhodium nitrate/nitrite complex. Thus, the nitrosyl species may originate from the decomposition of the rhodium nitrate/nitrite complex and subsequent reaction with NO. The nitrosyl species formed must be coordinated to the silica in a similar fashion to **2** since only the rhodium μ-oxo carbonyl complex **1** is regenerated, according to IR analysis. Alternatively, if the nitrosyl species originates from reaction of NO with **2**, then, by the same argument, decomposition of the rhodium nitrate/nitrite complex and subsequent reaction with NO must result in the formation of **2** or a complex similarly coordinated to the surface. Unfortunately, we cannot distinguish between these two pathways, but IR analysis demonstrates that the formation of the nitrosyl species cannot be

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[22] Schwartz, J.; Woolery, G., personal communication.

due solely to coordination of NO to **2**. The IR absorption at 1890 cm^{-1} denotes linear coordination of the nitrosyl ligand to the rhodium metal center.[21] According to the initial EXAFS analysis,[20] coordination of NO to **2** would result in a six-coordinate $\{MNO\}^8$ complex which would require the nitrosyl ligand to adopt a bent configuration.[23] Therefore, if **2** is the source of the nitrosyl species, either loss of the oxygen adduct ligand or a reversible change in surface coordination must occur. At this time, there is no evidence to rule out either effect.

4. Summary

Reaction of the μ-oxo carbonyl complex **1** with 30 Torr of NO at 100 °C resulted in the formation of the rhodium oxygen adduct **2** (80%) and rhodium nitrate/nitrite complex (20%) and was characterized by IR analysis and XPS. Comparison of the Rh $3d_{5/2}$ binding energies of **2** prepared via reaction of **1** and O_2 (310.1 eV) and of the NO-treated sample (310.1 eV) demonstrated the two to be identical within experimental error. XPS corroborated both the lack of nitrosyl coordination seen in IR and the sample's similarity to **2** in its reactivity for CO. The rhodium nitrate/nitrite complex was identified by IR (ν_{NO} = 1540 cm^{-1}), and an alternate assignment of this species to a carbonate complex was refuted by a ^{13}CO labeling experiment. No other nitrogen-containing products, either coordinated to the rhodium metal center or in the gas phase (e.g., N_2O), were observed by IR analysis. However, IR did detect CO_2 formation, which suggests that N_2 may be the primary nitrogen-containing product in this reaction.

Reaction of **1** with 70 Torr of NO at 400 °C was monitored by IR analysis. Both the decomposition of the rhodium nitrate/nitrite complex and the appearance of a nitrosyl species were observed. The nitrosyl species possessed a linearly coordinated NO ligand (ν_{NO} = 1890 cm^{-1}). Upon cooling and evacuation, the intensity of this absorption significantly decreased.

After the carbonyl complex **1** had been reacted with 30 Torr of NO at 100 °C, generating **2** and the nitrate/nitrite complex, **1** was regenerated from **2** by reaction with 30 Torr of CO at 100 °C. The rhodium nitrate/nitrite complex was unreactive toward CO under these conditions. More significantly, even after **1** had been reacted with 70 Torr of NO at 400 °C and formation of the nitrosyl species was observed, **1** was identified by IR as the primary product after treatment of the sample with 30 Torr of CO at 100 °C. In contrast to several of the previous investigations, only trace amounts of rhodium isocyanate, accounting for less than 2% of the total rhodium in the sample, was identified by IR analysis (ν_{NCO} = 2204 cm^{-1}). Formation of the isocyanate complex has been traced to the presence of rhodium aggregates; in separate experiments, conversion of dimeric complex **2** to a larger rhodium aggregate by treatment with H_2 resulted in a much greater yield of the isocyanate complex (27%) under milder reaction conditions.[24] In addition to decreasing the amount of active rhodium in the sample, isocyanate complex formation is undesirable since exposure to water will produce ammonia, which is tightly held and poisons the complex.[25] The ability to regenerate **1** demonstrates the integrity of the silica bonding and coordination to the rhodium metal center under the aforementioned reaction conditions. The catalytic behavior of these silica-attached rhodium complexes toward NO reduction by CO merits investigation.

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Carbon K-Shell Excitation of Metallocenes

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Abstract: The C 1s oscillator strength spectra of $M(C_5H_5)_2$, M = Fe, Co, and Ni, have been derived from inelastic electron scattering spectra under conditions dominated by electric dipole transitions. The region below the C 1s ionization potential in each spectrum is dominated by two peaks which are assigned to C 1s $\rightarrow 4e_{1g}(d_{xz},d_{yz})$ and C 1s $\rightarrow 3e_{2u}(\pi^*)$ excitations. These spectra are dramatically different from that expected for the C 1s spectrum of the free cyclopentadienyl radical or the cyclopentadienyl anion, either of which should be dominated by a single, low-lying $1s \rightarrow \pi^*$ transition. The intensity of the lower energy C 1s $\rightarrow 4e_{1g}$ transition is strongly dependent on the metal atom because of changes in the ground-state electron configurations. The results of extended Hückel theory calculations of the ground and C 1s excited states are found to be in qualitative agreement with the experimental results. The metallocene spectra are the first unambiguous experimental evidence for strong modification by metal bonding of the core excitation spectrum of a ligand. The spectra show that site-selective inner-shell excitation is a highly sensitive probe of the character of the unoccupied and partially filled molecular orbitals of organometallic compounds.

1. Introduction

Considerable attention is now being given to the electronic spectroscopy of organometallic compounds on account of their interesting and varied electronic structures and because they are useful models for the bonding of organic compounds to metal surfaces. Since the metallocene ("sandwich") compounds were discovered in 1951,[1] their electronic structure has been extensively studied by calculation[2] and by most standard spectroscopies. Spectroscopic studies of the unoccupied levels include electron transmission spectroscopy (ETS)[3,4] and valence excitation in the

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